Supramolecular ABA Triblock Copolymers via a Polycondensation Approach: Synthesis, Characterization, and Micelle Formation

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ABSTRACT: The combinatorial optimization of the reaction conditions of 1,16-bis(2,2′:6′,2″-terpyridin-4′-yloxy)-hexadecane **1** with $RuCl_3$ under reductive conditions to form supramolecular polymers with a bis-tpy-Ru(II) type connectivity, utilizing gel permeation chromatography as well as UV/vis spectroscopy as screening tools, led to an improved understanding of important polymerization parameters. Moreover, the obtained knowledge could be applied to the designed synthesis of an A-*b*-B-*b*-A type supramolecular triblock copolymer utilizing a α-terpyridine-ω-methyl-poly(ethylene glycol) polymer as a chain stopper during the polycondensation-like reaction. The resulting triblock copolymer revealed a composition of approximately 33 repeat units of **1**, outlining the value of the applied optimized conditions for its synthesis. Furthermore, it was observed that the synthesized triblock copolymer was able to form micelles in water. Finally, these micelles were investigated by dynamic light scattering, atomic force microscopy, as well as transmission electron microscopy.

Introduction

Polymers that contain supramolecular binding units are nowadays easily synthetically accessible. These supramolecular polymers can generally be defined as polymer chains of small molecules held together via reversible, noncovalent bonds.[1,2] The most prominent examples of supramolecular polymers can be found in hydrogen bonded systems and in systems that utilize metal ligand interactions. These examples include a large variety of different polymer architectures, such as dendrimers,[3,4] rods,[5] linear chain extended polymers,[6−8] copolymers,[9,10] block copolymers,[11,12] or graft copolymers.[13] In addition to the mentioned systems, a variety of different interactions, such as host−guest chemistry[14] or halogen bonding,[15] were shown to be useful for the construction of supramolecular polymers. Moreover, several examples have demonstrated that these new materials can provide interesting properties including, for instance, thermo-, chemo-, and mechanoresponsive supramolecular polyelectrolyte gel-like materials that show thixotropic behavior[16] or star-shaped supramolecular polymers that can encapsulate dye molecules and act as fluorescent sensors due to the binding of transition metal ions to terpyridine receptors.[17]

For the class of metal coordinating polymers, terpyridine−metal complexes are particularly widely applied as building blocks in supramolecular and macromolecular chemistry. In principle, all architectures that are known for classical polymers should also be realizable by applying the terpyridine−metal complexation chemistry.[18,19] For instance, it has been reported that the preparation of well-defined block copolymers is feasible via selective mono-complex formation of Ru(III)-ions with terpyridine ligands and subsequent reaction with a second terpyridine ligand (under reducing conditions) leading to block copolymer systems with a large variety of different polymeric building blocks.[11,20] The micellar properties[20,21] of such systems are of particular interest since it is, for instance, possible to cleave the corona of the micelles with competitive ligands to obtain defined nano-objects composed of the micellar core material.[22] This is an interesting example of how the presence of supramolecular binding units can be utilized to prepare new materials that would otherwise be difficult to access.

As was already mentioned, it should be possible to create all traditional polymer architectures utilizing supramolecular interactions as connections between polymer chains of various sizes and compositions. Within this paper, we describe a new synthetic approach for the preparation for supramolecular A-*b*-B-*b*-A triblock copolymers utilizing polycondensation chemistry and thereby expanding the accessible range of terpyridine-based supramolecular polymer architectures. First, the reaction conditions were optimized for the polymerization of a flexible bis-terpyridine ligand regarding, for instance, temperature, concentration, and type of additives in a parallel fashion utilizing a carousel reactor. This manual parallel approach was best suited for the quick evaluation of the desired polymerization features.[23] The applied screening techniques were a specially developed gel permeation chromatography (GPC) system[24] capable of investigating different kinds of metal−ligand based supramolecular polymers and a parallel UV/vis plate reader setup. This combination allowed a fast evaluation of the important parameters, namely, the relative molecular weight as well as the UV characteristics of the obtained polymers. Finally, the knowledge gained from these screening experiments was applied to the synthesis of supramolecular A-*b*-B-*b*-A triblock copolymers with water-soluble poly(ethylene glycol) (PEG) A blocks and a water-insoluble metal-containing B block. This ABA triblock copolymer revealed amphiphilic properties, and it was possible to prepare water soluble micelles that were investigated by means of dynamic light scattering (DLS), atomic force microscopy (AFM), and transmission electron microscopy (TEM) methods.

Experimental Procedures

Chemicals and Reagents. Basic chemicals were obtained from Sigma-Aldrich (Oakville, ON). 4′-Chloro-2,2′:6′,2″-terpyridine was

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synthesized according to a literature procedure.[25] Analytical and HPLC grade solvents were purchased from Biosolve LTD (Valkenswaard, The Netherlands).

Instrumentation. Gel permeation chromatograms were measured on a Waters GPC system consisting of an isocratic pump, solvent degasser, column oven, 2996 photodiode array (PDA) detector, 2414 refractive index detector, 717plus autosampler, and a Styragel HT 4 GPC column with a precolumn installed. The eluent was *N*,*N*-dimethyl formamide (DMF) with 5 mM NH_4PF_6 at a flow speed of 0.5 mL/min. The column temperature was 50 °C.

UV/vis spectra were recorded on a FlashScan 530 (AnalytikJena, Germany) in 96-well microtiter plates (polypropylene, flat bottom) from Greiner (Greiner Bio-One, Germany) in a range from 250 to 800 nm. All spectra were referenced to an empty microtiter plate, and measurements were performed with four flashes. The actual time for the measurement of one microtiter plate with 96 full UV/vis spectra was approximately 40 s.

NMR spectra were measured on a Bruker Mercury 400 NMR spectrometer in various deuterated solvents. The chemical shifts were calibrated to TMS.

Dynamic light scattering (DLS) experiments were performed on a Malvern CGS-3 equipped with a He−Ne laser (633 nm). The measurements have been performed at an angle of 90° and at a temperature of 25 °C. The polydispersity index was calculated from the μ_2/Γ_1^2 ratio, where μ_2 is the second cumulant and Γ_1 is the first cumulant from a cumulant analysis of the DLS data.

AFM imaging in liquid was performed using an Ntegra SPM (NT-MDT, Moscow) and AC40TS-type (SiN, 0.1 N/m, Olympus, Tokyo) cantilevers. To avoid tip convolution effects, the diameter of the micelles was estimated from the observed height.

Transmission electron miscrocopy (TEM) was performed on a LEO 922 microscope, operating at a 200 kV accelerating voltage in bright-field mode. The images were formed by unscattered electrons only. Samples for TEM experiments were prepared by spin-coating a drop of diluted solution of micelles on a carbon-coated TEM grid. The samples for TEM measurements were not stained.

GPC and UV/vis Screening. Samples (20 μL for each measurement) were taken directly from the reaction mixtures at various times and diluted with GPC eluent to a volume of 1 mL for GPC measurements or diluted with DMF to 250 μL in polypropylene microtiter plates for UV/vis measurements. Subsequently, UV/vis spectra were recorded in parallel, whereas GPC samples were transferred to the autosampler of the GPC system to be measured and processed.

Synthesis of 1,16-bis(2,2′:6′,2″-Terpyridin-4′-yloxy)hexadecane (1). Compound **1** was prepared according to a modified literature procedure.[26] To a stirred suspension of powdered KOH (449 mg, 8 mmol) in dry DMSO (25 mL) at 60 °C 1,16-hexadecanol (517 mg, 2 mmol) was added. After 15 min, 4′-chloro-2,2′:6′,2″-terpyridine was added (1.17 g, 4.4 mmol), and the mixture was stirred for 24 h at 60 °C and subsequently poured into cold water (600 mL). The product precipitated and was collected by filtration and afterward washed with deionized water and methanol. After drying in vacuo, **1** was obtained as a white solid (1.26 g, 85%). ^{1}H NMR ($CDCl_3$): δ = 1.25−1.42 [m, 20 H, $OCH_2CH_2CH_2(CH_2)_{10}CH_2CH_2CH_2O$, 1.50 [tt, 4 H, J = 8.1, 7.3 Hz, $OCH_2CH_2CH_2$], 1.85 [tt, 4 H, J = 7.3, 6.6 Hz, OCH_2CH_2], 4.22 [t, 4 H, J = 6.6 Hz, OCH_2], 7.32 [m, 4 H, H5,5″], 7.84 [m, 4 H, H4,4″], 8.01 [s, 4 H, H3′,5′], 8.61 [d, 4 H, J = 8.1 Hz, H3,3″], 8.69 [d, 4 H, J = 3.7 Hz, H6,6″]. MALDI-TOF-MS: (matrix: dithranol): m/z (%) = 721.9 (MH^+, 35%), 743.9 (MNa^+, 100%).

Screening Polymerizations of 1. Compound **1** was polymerized with $RuCl_3$ in various stoichiometries and under diverse conditions in a 12-place carousel reaction station from Radleys. Different solvents, temperatures, reactant ratios as well as various additives, such as different salts and different alcohols, were investigated.

Synthesis of α-Terpyridine-ω-methyl-poly(ethylene glycol) (2). Compound **2** has been prepared according to literature procedures.[27] ^{1}H NMR ($CDCl_3$): δ = 3.57 [s, 260 H, PEG-backbone], 4.4 [t, 2 H, J = 6.6 Hz, tpy-OCH_2], 7.32 [m, 2 H, H5,5″], 7.84 [m, 2 H, H4,4″], 8.01 [s, 2 H, H3′,5′], 8.61 [d, 2 H, J = 8.1 Hz, H3,3″], 8.69 [d, 4 H, J = 3.7 Hz, H6,6″]. MALDI-TOF-MS: (matrix: dithranol): M_n = 3025, PDI = 1.01. GPC: M_n = 3030, PDI = 1.07.

Synthesis of bis-(α-Terpyridine-ω-methyl-poly(ethylene glycol))Ru(II) (3). $RuCl_3$ (0.12 mmol, 24.9 mg) and **2** (0.12 mmol, 360 mg) were added to a solvent mixture of dimethylacetamide (DMA) (414 μL), *n*-butanol (110 μL, 1.2 mmol, 88.9 mg), and *N*-ethyl-morpholine (76 μL, 1.2 mmol, 69.1 mg) utilizing a conical glass vial that can be capped with a septum. The reaction was performed for 5 h at 130 °C. The product was purified by preparative size-exclusion chromatography (BioBeads SX-1, dichloromethane). Analytical results were according to the literature values.[27]

Synthesis of Supramolecular ABA Triblock Copolymer (4). $RuCl_3$ (0.132 mmol, 27.4 mg), **1** (0.12 mmol, 86.5 mg), and **2** (0.012 mmol, 36 mg) were added to a solvent mixture of dimethylacetamide (DMA) (396 μL), *n*-butanol (121 μL, 1.32 mmol, 97.8 mg), and *N*-ethyl-morpholine (83 μL, 1.32 mmol, 76.0 mg) utilizing a conical glass vial that can be capped with a septum. All components became readily dissolved after stirring the mixture for 3 min at 70 °C. The polymerization was performed for 5 h at 130 °C. The resulting product was first precipitated in acetone and then redissolved in methanol. NH_4PF_6 was added in 10-fold excess, and the mixture was refluxed for 1 h. After cooling to room temperature, **4** precipitated and was collected by filtration. Excess NH_4PF_6 was removed by preparative size-exclusion chromatography (BioBeads SX-1, acetone), yielding **4** as a red powder (105 mg, 59%). ^{1}H NMR (acetone-d_6): δ = 1.25−1.55 [m, 792 H, $OCH_2CH_2CH_2(CH_2)_{10}CH_2CH_2CH_2O$ and $OCH_2CH_2CH_2$], 1.67 [m, 132 H, OCH_2CH_2], 3.57 [s, 480 H, PEG-backbone], 4.62 [t, 136 H, J = 6.6 Hz, OCH_2], 7.31 [m, 136 H, H5,5″], 7.74 [d, 136 H, J = 5.1 Hz, H6,6″], 8.03 [t, 136 H, J = 8.1 Hz, H4,4″], 8.68 [s, 136 H, H3′,5′], 8.82 [d, 136 H, J = 8.1 Hz, H3,3″].

Micelle Preparation. The metallo−supramolecular polymer **4** is insoluble in water. Therefore, it was first dissolved in an unselective solvent, such as dimethyl sulfoxide (DMSO) or acetone, and subsequently, an at least 50-fold excess of deionized water was added dropwise while being stirred. The resulting micellar solution was dialyzed several times against pure deionized water to remove the residual unselective solvent. The resulting micellar solutions had a concentration of approximately 1 wt %.

Results and Discussion

Polymers that contain supramolecular binding units are an interesting field of research, and their study has led to several new functional materials (see, e.g., refs 16 and 17). In particular, terpyridine (tpy) metal complexes are widely used as building blocks in supramolecular and macromolecular chemistry resulting in a large variety of different supramolecular polymer architectures.[18,19] We investigated the one-step polymerization of 1,16-bis(2,2′:6′,2″-terpyridin-4′-yloxy)hexadecane **1** with $RuCl_3$ under reducing conditions in a parallel fashion to optimize the reaction conditions for this polymerization process. This was necessary since known literature procedures for the polymerization of bis-terpyridine ligands require (very) long reaction times and/or an additional step for the activation of the ruthenium species.[6,28] Subsequently, we applied the gained knowledge to the preparation of a supramolecular ABA triblock copolymer that might show interesting material properties, such as the formation of micelles due to its amphiphilic character. However, as a first step of investigations, the reaction of **1** (and other tpy compounds) with $RuCl_3$ had to be investigated in more detail to avoid time-consuming procedures and to obtain better control of the polymerization procedure. Therefore, the polymerization conditions of 1,16-bis(2,2′:6′,2″-terpyridin-4′-yloxy)-hexadecane with $RuCl_3$ were optimized utilizing a carousel reactor. This parallel approach allowed the fast investigation

Table 1. Screening Data for Six Polymerization Runs of Monomer 1 with $RuCl_3$ (1:1 Molar Ratio, 2:1 Ratio of tpy/Ru) under Various Conditions at 130 °C[a]

	additive	*c*(**1**) (mmol/mL)	conversion of **1** after 24 h[b] (%)	λ_{max} UV/vis (nm)
1		0.02	<10	490
2	Ethanol	0.02	15	400, 440, 490, 530
3	NH_4PF_6/butanol	0.02	<10	none
4	***N***-ethyl-morpholine/butanol	0.01	27	490
5	***N***-ethyl-morpholine/butanol	0.03	39	490
6	*N*-ethyl-morpholine/butanol	0.2	80−85 (after 5 h)	490

[a] All additives are in 10-fold excess according to **1**. [b] Conversions are estimated based on GPC screening results.

of different additives and concentrations for the polymerization procedure. All polymerizations were monitored by GPC as well as UV/vis spectroscopy, aiming for an as high as possible molecular weight and monomer conversion while maintaining the typical UV/vis characteristics of the bis-tpy-Ru(II) complex (e.g., the pronounced MLCT band at ~490 nm). It should be noted here that ruthenium was chosen because it forms very stable complexes with terpyridine ligands, thereby offering the possibility of investigating the obtained species by an optimized GPC method.[24] Other transition metal ions, such as Co^{2+}, Cu^{2+}, Fe^{2+}, and others, do also form stable complexes with terpyridine ligands.[29] However, to our experience, they are not stable enough for an investigation by means of GPC chromatography. Nevertheless, even the choice of the very stable ruthenium complexes allows the opening of complexes after their synthesis utilizing, for example, redox chemistry.[30] The first results of these screening reactions revealed that dimethylacetamide (DMA) was a suitable, high boiling solvent for this kind of polymerization[28] that does not show undesired side reactions and dissolves the monomer, $RuCl_3$, as well as the resulting polymer very well at elevated temperatures.

Table 1 summarizes representative results of the more than 20 performed optimization reactions. Generally, the polymerizations in DMA proceeded without any additives, however, only very slowly reaching ca. 5−10% conversion after 24 h of reaction time (compare Table 1, entry 1). The addition of alcohols such as ethanol or butanol slightly increased the observed conversions and molecular weights but led to undefined species as observed by UV/vis spectroscopy (compare Table 1, entry 2). The addition of *N*-ethyl-morpholine had no effect on the polymerization speed. Furthermore, the addition of salts that could maybe promote an exchange of the counterions of the obtained bis-tpy complexes such as NH_4PF_6 or $AgBF_4$ did not affect the observed conversions. The addition of salt and alcohol to a reaction mixture led to the formation of undefined complexes without characteristic features in the UV/vis spectrum (compare Table 1, entry 3). The possibility of the formation of defect structures in tpy complexes with ruthenium(II) ions was already discussed in the literature[28] and might be due to the fact that the counterions that are present during the complex formation coordinate to the ruthenium center. Nevertheless, the addition of alcohol and *N*-ethyl-morpholine led to the formation of high molecular weight species with the desired UV/vis characteristics (MLCT band of the bis-Ru(II)-terpyridine complex at 490 nm) providing high monomer conversions. However, the addition of triethylamine and butanol did not lead to high conversions and high molecular weight species. Furthermore, Table 1, entries 4 and 5 reveal that an increase in the concentration of **1** resulted in increased conversions. Further investigating that effect showed that a polymerization performed with a monomer concentration of 0.2 mmol/mL at 130 °C for 5 h provided a monomer conversion of 80−85% as estimated by both ^1H NMR and GPC analysis (Table 1, entry 6). These results, in combination with a good reproducibility of the performed reactions, led us to the conclusion that DMA in combination with butanol and *N*-ethyl-morpholine as reducing additives is a very capable reaction medium for the polymerization of **1** with $RuCl_3$ under reducing conditions. Moreover, utilizing these conditions it was observed that lower monomer concentrations led to lower molecular weights of the obtained polymers. This behavior is consistent with polymerization theory and can be explained by a favored intermolecular reaction of the reactive polymer chain ends at higher concentrations.

Figure 1 displays GPC results for two polymerizations performed at 130 °C in DMA for 24 h. It is obvious that the increase in monomer concentration from 0.01 to 0.17 mmol/mL led to the formation of higher molecular weight species and moreover to an increase in the observed monomer conversion. However, it is also clearly visible that a mixture of different species was obtained, which are most likely different sizes of macromolecular rings and linear polymers (compare Scheme 1). Such macromolecular rings were isolated by different authors[26,31] but not further investigated here. In the course of further investigations, it was observed that a monomer concentration of 0.2 mmol/mL with a 10-fold excess of butanol and *N*-ethyl-morpholine as additives in capped conical vials led to the highest molecular weights and largest conversions after a reasonable reaction time of 5 h. Higher concentrations of monomer could not be applied due to solubility problems. The capped vials were utilized to avoid any loss of the lower boiling butanol during the reaction. Moreover, the optimized conditions were also tested on different (also rigid) bis-tpy ligands, and the conditions generally offer very good results. Further investigations in that direction will be reported elsewhere. In conclusion, the optimized reaction conditions represent a crucial improvement over literature procedures since the polymerization time could be reduced from 5 days to 5 h and since no precipitation was observed during the reaction.[28]

After the evaluation of the best reaction conditions for the polymerization of 1,16-bis(2,2′:6′,2″-terpyridin-4′-yloxy)hexadecane **1** with $RuCl_3$, the supramolecular ABA triblock copolymers could be synthesized via a polycondensation approach utilizing a α-terpyridine-ω-methyl-poly(ethylene glycol) polymer **2** as a chain stopper during the polymerization reaction (see Scheme 1). As a consequence, both ends of the synthesized polymer will be capped with poly(ethylene glycol) chains resulting in the desired A-*b*-B-*b*-A structure. Moreover, the utilization of a chainstopper in the course of the polymerization will avoid the formation of macrocyclic rings to a large extent. The most promising results were obtained in the presence of 10 mol % **2** with respect to **1** and the corresponding amount of $RuCl_3$ within a 5 h reaction time. The crude polymer was precipitated in acetone, and subsequently, the counterions were exchanged from Cl^- to PF_6^- by refluxing the polymer with an excess of NH_4PH_6 in methanol. This led to the precipitation of the supramolecular triblock copolymer **4** (see Scheme 1) upon cooling. It should be mentioned here that only changing the counterions had a significant effect on the solubility of the

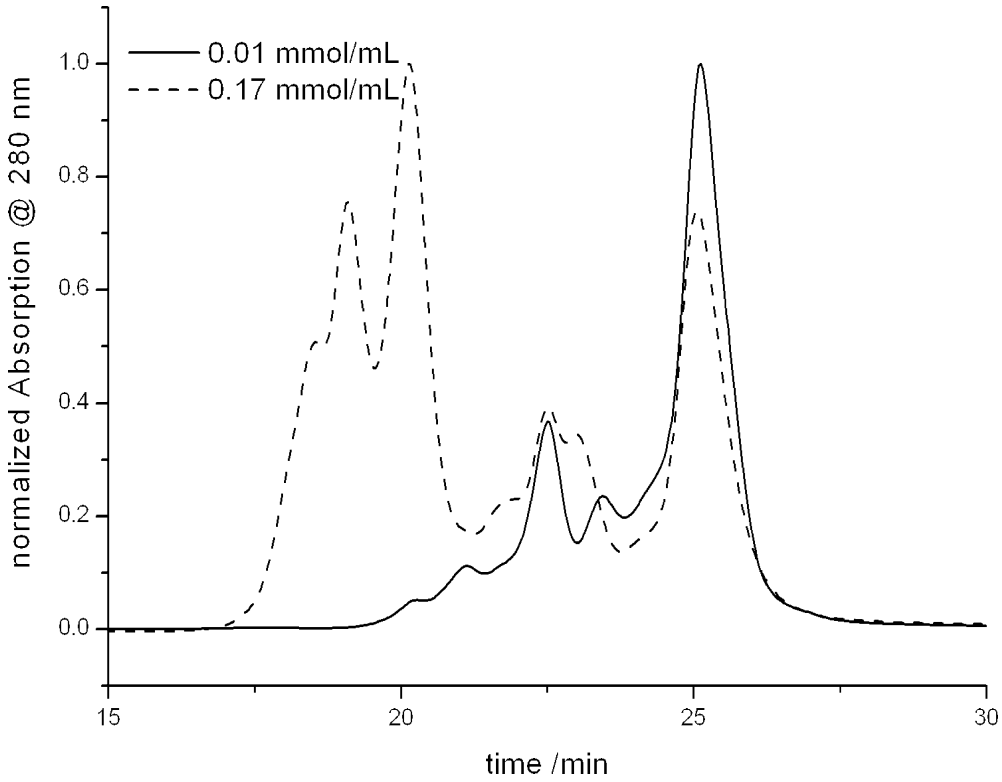
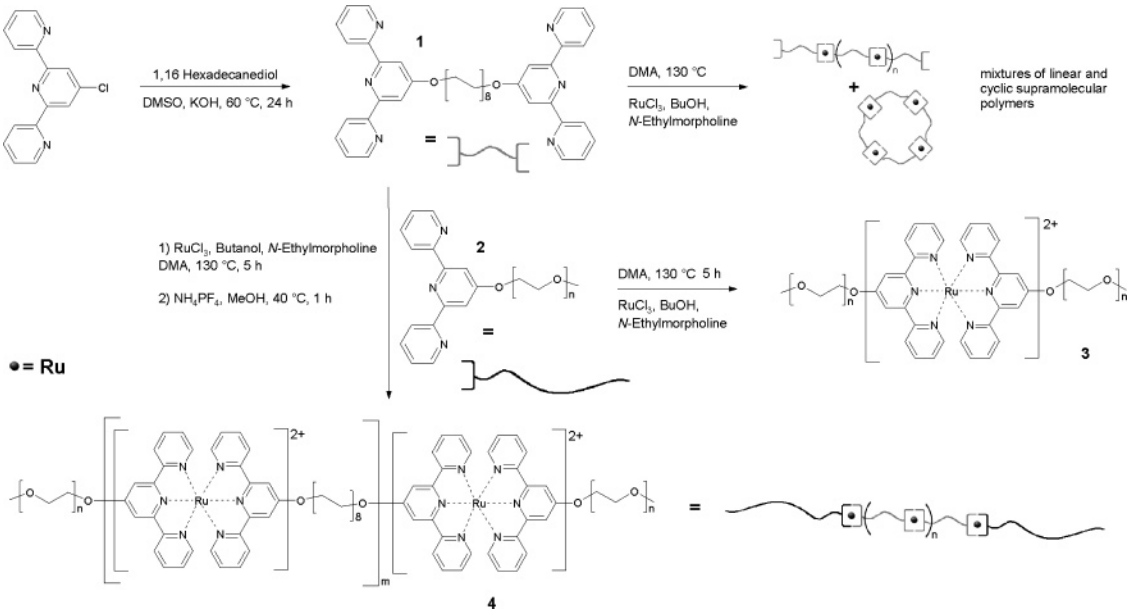


Figure 1. UV/vis chromatograms of two supramolecular polymerization reactions of 1,16-bis(2,2′:6′,2″-terpyridin-4′-yloxy)hexadecane **1** illustrating the concentration effect on the polycondensation-like polymerization procedure.

Scheme 1. Overview of Performed Polymerization and Optimization Reactions Finally Leading to Synthesis of Supramolecular ABA Triblock Copolymer 4[a]



[a] Counterions are omitted for simplicity reasons.

synthesized polymer: with chloride counterions, it was methanol soluble and acetone insoluble, whereas with hexafluorophosphate counterions, the reverse behavior was observed. Recently, it was also reported that an exchange of the counterions of a bis(terpyridine)ruthenium(II) complex that connects a poly(styrene) block with a PEG block in a diblock copolymer led to a change in the melt morphology from a spherical to a lamellar mesophase.[32] These are interesting examples of how the properties of a metal containing polymer can be changed by a simple exchange of its counterions outlining the additional freedom these types of polymers offer for the tailoring of polymer properties. In the case of polymer **4**, the exchange to PF_6^- counterions changed its solubility completely, making it water insoluble (also upon heating or ultrasonication).

Figure 2 displays the chromatogram of polymer **4** obtained with a photodiode array detector revealing the characteristic $(tpy)_2$-Ru MLCT band at 490 nm over the whole polymer distribution. The insets show a UV chromatogram at an absorption wavelength of 310 nm and a UV/vis spectrum at an elution time of 17.5 min, respectively. Moreover, it was observed (see Figure 3) that polymer **4** eluted faster than polymer **3** (compare Scheme 1), indicating its higher molecular weight.

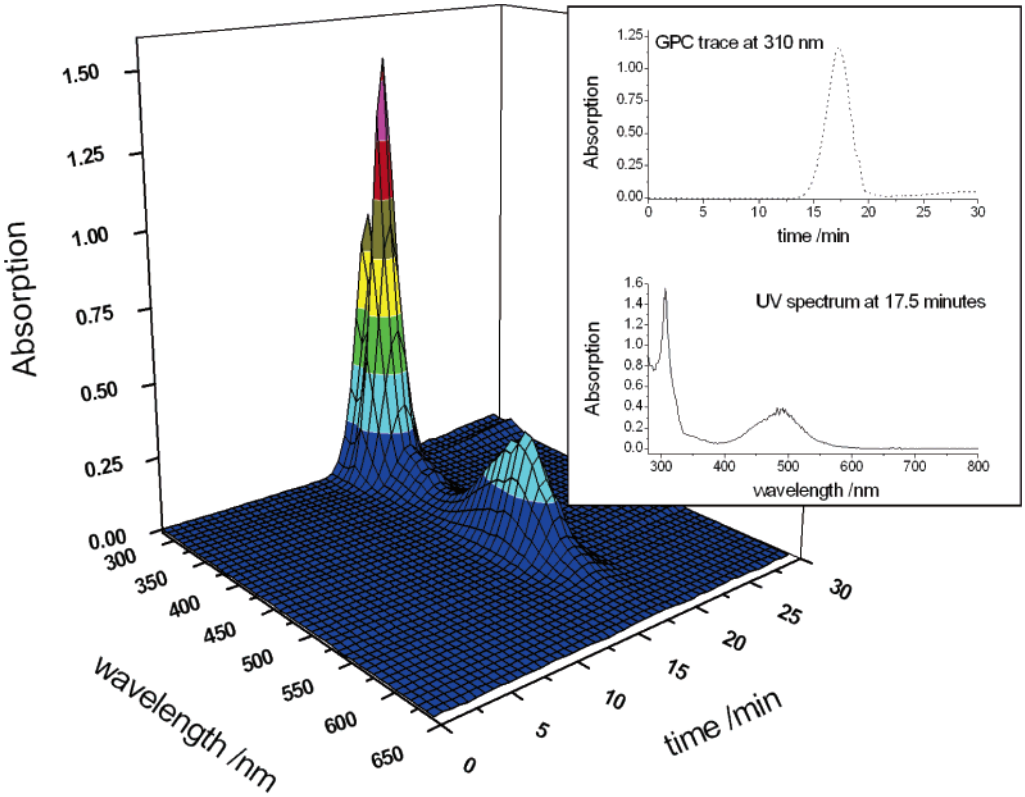


Figure 2. Photodiode array gel permeation chromatogram results after workup of polymer **4**.

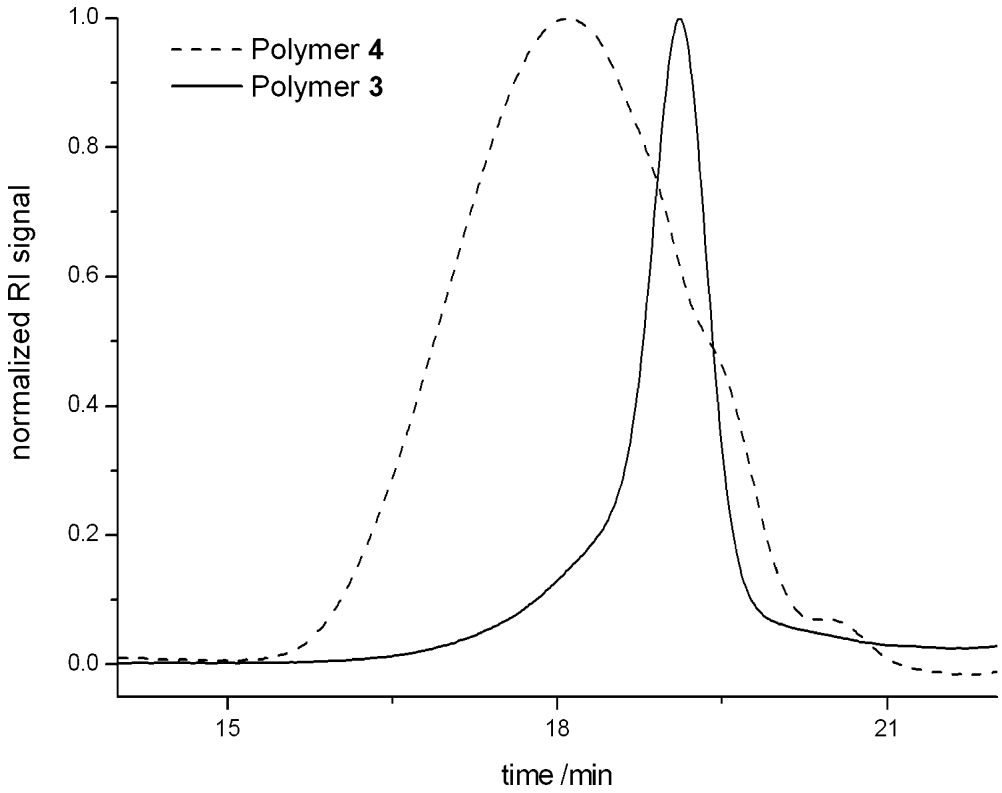


Figure 3. Gel permeation chromatography traces of polymers **3** and **4**.

However, no suitable calibration was found until now to evaluate the molecular weight of the supramolecular polymer **4** by means of standard GPC techniques. As a point of discussion, molecular weight values of polymers **3** and **4** utilizing different calibrations are provided in Table 2. It was observed that the PEO calibration shows comparable molecular weight values to ^{1}H NMR calculations for polymer **3** but underestimates the molar mass of the central B block in polymer **4** since approximately 30 repeat units of **1** are expected in polymer **4** (compare the following ^{1}H NMR results and Table 2). Moreover, both PS and PMMA calibrations are absolutely not suitable for an evaluation of the molecular weight of polymer **3** since they largely overestimate its M_n. The PS calibration, on the other hand, seems to be well-suited for molar mass estimations of the central block of **4** since the

Table 2. Molecular Weight Values for Polymers 3 and 4 Obtained Utilizing Different Calibrations for GPC Analysis

polymer/calibration	M_n (g/mol)	M_w (g/mol)	PDI	repeat units of **1**[a]
3/PEG	8450	10200	1.21	
4/PEG	18400	34200	1.86	9
3/PS	36300	40000	1.10	
4/PS	68700	94600	1.38	29
3/PMMA	20700	23300	1.13	
4/PMMA	40200	59600	1.48	18

[a] The number of repeating units of **1** was calculated from the difference of M_n values of polymer **3** and **4** utilizing the respective calibrations.

calculated repeat unit number of 29 is very close to values obtained by ^{1}H NMR spectroscopy. However, even if none of the applied GPC calibrations are suitable for **4** with DMF as eluent, all results clearly demonstrate the increase in both the molecular weight and the polydispersity index of **4** if compared to **3**.

Figure 3 also clearly depicts that polymer **4** shows two small shoulders at the low molecular weight side of its molecular weight distribution, which are most likely due to the presence of a minor fraction of macromolecular rings and/or polymer **4** that was only functionalized with PEG on one side resulting in an AB block copolymer-like structure. In addition, a broadening of the molecular weight distribution of **4** (PDI $\sim$ 1.6, average of PEO and PS calibration), if compared to **3** (PDI $\sim$ 1.2, PEO calibration), can be observed. Both observations were expected since it is known for many different kinds of polycondensations that cyclic species are formed in different amounts (see, e.g., refs 33−35 for recent examples), and a polydispersity index of 2 is expected for 100% functional group conversion if the classic theory developed by Flory is taken into account.[36,37] A detailed ^{1}H NMR analysis of **4** (compare Figure 4) revealed that the terpyridine signals of monomer **1** as well as of the terpyridine modified PEG shifted upon complexation with ruthenium ions and that the obtained polymer only shows complexed terpyridine signals. This is a clear indication that the shoulders observed in the GPC trace of **4** (compare Figure 3 and the previous discussion) are due to macrocyclic rings and not an A-*b*-B type supramolecular polymer since the latter would show signals of free terpyridine moieties in the ^{1}H NMR spectrum. End-group calculations utilizing the PEG polymer as an end-group and assuming that both ends of polymer **4** were functionalized with PEG reveal that on average, 33 of the 1,16-bis(2,2′:6′,2″-terpyridin-4′-yloxy)hexadecane units were built into the polymer backbone. Therefore, the number average molecular weight of polymer **4** can be calculated to be 43 kDa (including counterions). These results demonstrate that it is feasible to construct supramolecular ABA triblock copolymers utilizing a one pot polycondensation approach applying the optimized reaction conditions.

To study the amphiphilic character of the obtained supramolecular triblock copolymer **4**, its ability to form micelles was investigated (Scheme 2). Since the supramolecular polymer was not readily soluble in water, pure water was added dropwise to a solution of **4** in DMSO or acetone, and the obtained solution was dialyzed against pure water, leading to frozen micelles. Details about this method are reported in the literature.[21] In short, the supramolecular polymer **4** is molecularly dissolved in the unselective solvent (as confirmed by ^{1}H NMR). Upon the addition of water, the solvent quality for the central supramolecular block decreases continuously, and aggregation is induced. At higher water contents, the mobility of the central B segment of polymer **4**, forming the core of the micelles, will be very low, and the process of polymer self-assembly and the equilibrium between micelles and individual polymer chains will be very slow. Finally, after dialysis of the residual unselective solvent, the micellar structure can be considered as kinetically

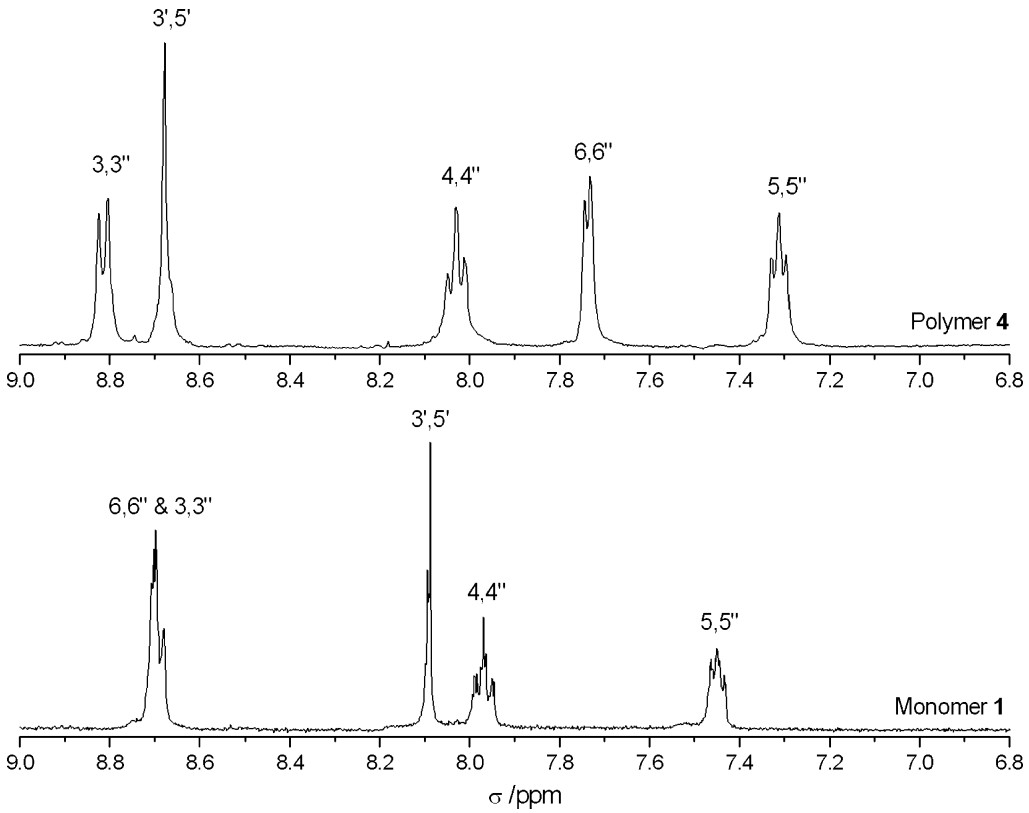


Figure 4. ^{1}H NMR analysis of monomer **1** and polymer **4** in acetone-d_6 revealing the typical shifts of terpyridine protons due to the complexation with ruthenium ions.

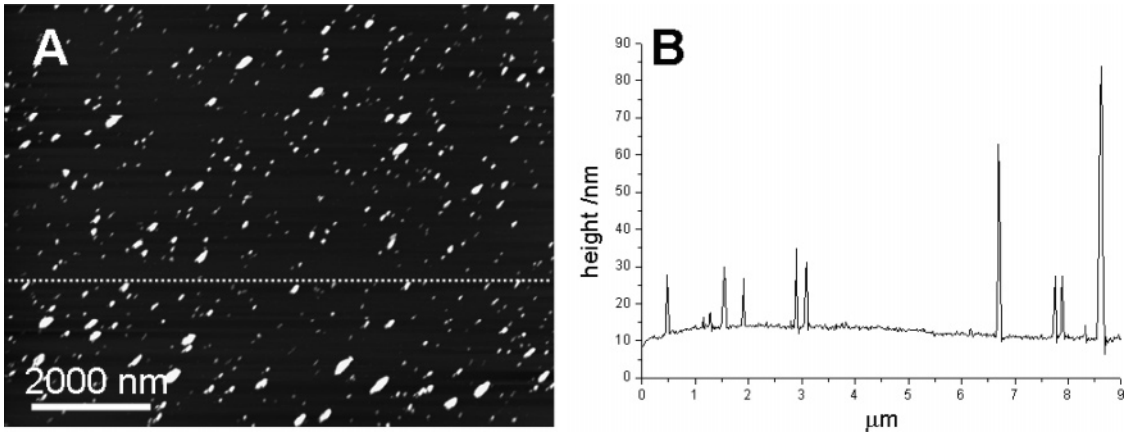


Figure 5. (A) Resonant mode topography image of micelles of **4** imaged in solution. Image *z*-range is 50 nm. (B) Cross-section taken at the position indicated by the dotted line. The average height of individual micelles was approximately 26 nm.

frozen. Therefore, micelles with a supramolecular metal−ion complex containing core and a PEG corona were obtained from triblock copolymer **4**. Dynamic light scattering of the obtained micelles showed the presence of objects with a diameter of 70 nm as well as a minor population of aggregates of these micelles with a size of approximately 500 nm. The polydispersity index obtained by DLS was 0.45, indicating that the micelles were rather polydisperse. Moreover, micelles of **4** have been imaged by resonant mode scanning probe microscopy in water. The measurements were performed by immersing the cantilever directly in the micelle solution of **4** in water. An image obtained in these conditions is presented in Figure 5, showing individual micelles as well as clusters of micelles. The micelles in their native environment showed a diameter of 26 nm on average (standard deviation: 6.5 nm). This result might be explained by the fact that the AFM tip penetrated the swollen PEG corona.[38] Furthermore, TEM experiments of unstained micelles revealed spherical objects with a mean diameter of 25 nm (compare Figure 6, standard deviation 5 nm). This result clearly shows that the investigated micelles have the proposed structure with the supramolecular repeat unit in the core of the micelles since (i) a repeat unit containing no metal would show no contrast in TEM and (ii) rings would be observed in the case where the metal containing repeat units would form the corona of the micelles. The investigation of the micelles of **4** with various techniques provided a good picture of their morphological characteristic features. The diameter of the core of the micelles (∼25 nm) was obtained by TEM and AFM. Finally,

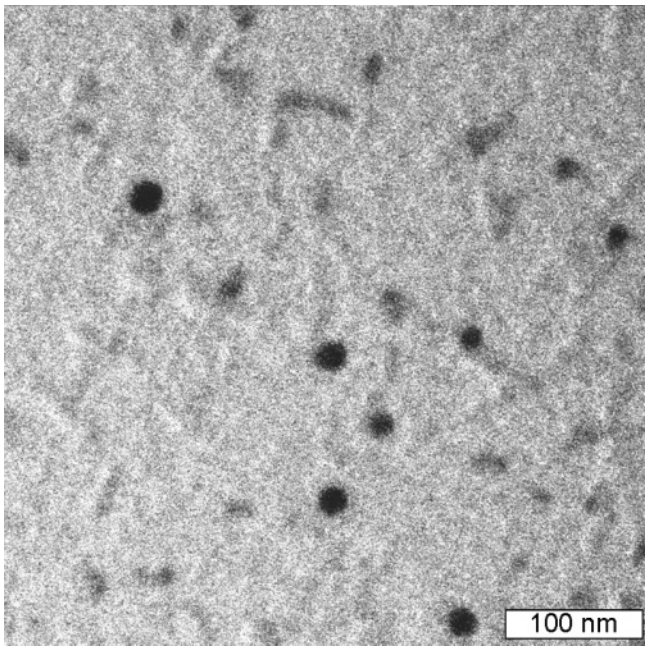
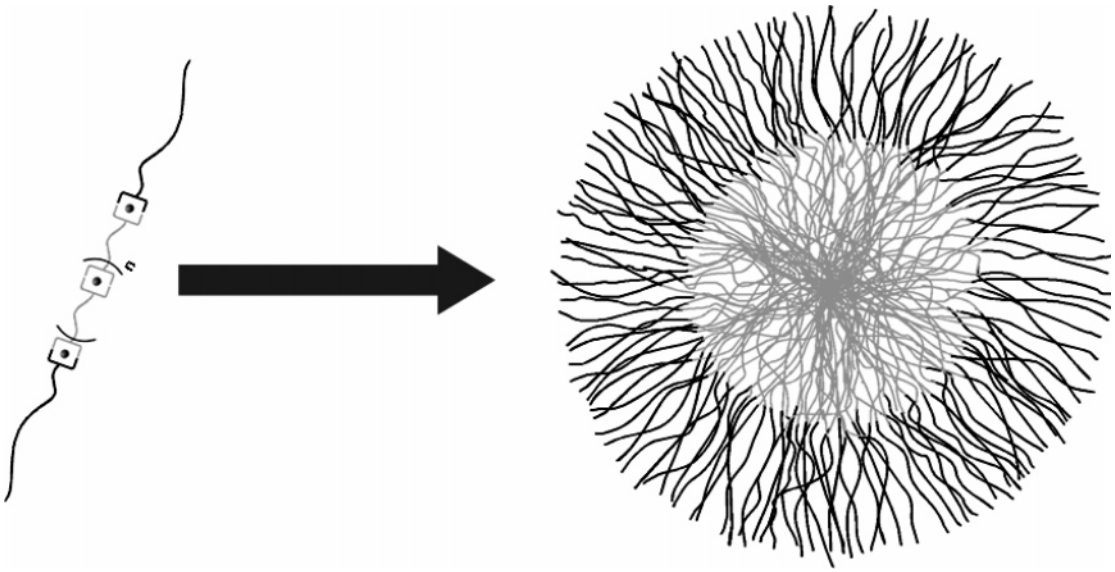


Figure 6. TEM image of micelles of **4** observed without staining.

Scheme 2. Schematic Representation of Micelle Formation of 4



the total size (core + corona) of the hydrated micelles can be estimated to be around 70 nm as measured by DLS.

Conclusion

We have shown that a parallel approach utilizing GPC as well as UV/vis as screening methods for the optimization of the polymerization conditions of **1** was successful and led to the designed synthesis of the supramolecular ABA triblock copolymer **4**. The optimized reaction conditions led to higher molecular weight polymers within a reduced polymerization time revealing the bis-tpyRu(II) type connectivity in its backbone. The triblock copolymer **4** was composed of approximately 33 repeat units of **1** outlining the usefulness of the applied optimized conditions for its synthesis. Furthermore, **4** proved to be amphiphilic, and we were able to prepare micelles from **4** in a straightforward approach. The resulting micelles were investigated utilizing DLS as well as AFM and TEM as imaging techniques. The obtained results demonstrate that it is possible to prepare ABA type block copolymer architectures utilizing the supramolecular terpyridine metal type of connectivity and open ways for the synthesis of novel kinds of block copolymer structures by (i) applying different kinds of terpyridine functionalized polymers as chain stoppers and/or (ii) applying different kinds of bis-terpyridine functionalized supramolecular monomers.

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